XIX. *On a New Series of Organic Bodies containing Metals.*
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UNDER the above title I described, more than three years ago, some preliminary experiments† which proved the existence of certain organic compounds highly analogous to cacodyl, and, like that body, consisting of a metal, or in some cases phosphorus, associated with the groups $C_2 H_3$, $C_4 H_5$, $C_6 H_7$, &c., and possessing, in most instances, highly remarkable powers of combination. I fixed the composition and studied some of the reactions of two of these bodies, to which the names Zincmethyl $(C_2 H_3 Zn)$ and Zincethyl $(C_4 H_5 Zn)$ were provisionally assigned, besides giving methods for procuring similar compounds containing tin, arsenic and phosphorus, by acting upon the iodides of the alcohol radicals with these elements, and expressing a belief, founded upon the similarity of functions existing between hydrogen and the groups of the form $C_n H_{(n+1)}$, that most, if not the whole, of the compounds contained in the following series might be formed; those marked thus * being at that time already known.

Hydrogen series.	Methyl series.	Ethyl series.	Butyl series.	Valyl series.	Amyl series.	Phenyl series.
Zn H	Zn $C_2 H_3$*	Zn $C_4 H_5$*	Zn $C_6 H_7$	Zn $C_8 H_9$	Zn $C_{10} H_{11}$	Zn $C_{12} H_5$
As H_2*	As $(C_2 H_3)_2$*	As $(C_4 H_5)_2$	As $(C_6 H_7)_2$	As $(C_8 H_9)_2$	As $(C_{10} H_{11})_2$	As $(C_{12} H_5)_2$
Sb H_3*	Sb $(C_2 H_3)_3$	Sb $(C_4 H_5)_3$	Sb $(C_6 H_7)_3$	Sb $(C_8 H_9)_3$	Sb $(C_{10} H_{11})_3$	Sb $(C_{12} H_5)_3$
P H_3*	P $(C_2 H_3)_3$*	P $(C_4 H_5)_3$	P $(C_6 H_7)_3$	P $(C_8 H_9)_3$	P $(C_{10} H_{11})_3$	P $(C_{12} H_5)_3$

More recently LÖWIG and SCHWEITZER‡ have commenced labouring in the same field, and have filled up one of the gaps in the foregoing table by the formation of stibethyl $(Sb(C_4 H_5))$, in acting upon iodide of ethyl with an alloy of antimony and potassium; the same chemists state also the probable formation of similar compounds containing methyl and amyl in place of ethyl, and bismuth and phosphorus instead of antimony.

I have continued my researches upon the organo-metallic bodies formed as above described, and having succeeded in increasing the list by the addition of several new members, I propose, in a series of papers, of which this is the first, to lay before the Royal Society the results of my experiments on the formation of bodies of this class.

The agents which I have hitherto employed in the formation of these organo-

metallic compounds are two, viz. heat and light; in many cases either of these can be used, in others only one can be made to effect the desired combination, whilst more rarely the assistance of both appears to be essential. In those experiments in which heat was employed the materials were subjected to its action in sealed glass tubes, about 12 inches long, and varying in diameter from half an inch to 1 inch, the thickness of the glass being about one-eighth of an inch*. To preserve the gaseous products of the operation in a state of perfect purity for subsequent investigation, the tubes were well exhausted before being sealed; they were then immersed to about half their depth in an oil-bath, and heated to the required temperature. In cases where the influence of light was employed, the materials, confined in tubes of precisely similar dimensions, were exposed to the sun's rays, concentrated in most cases by an 18-inch parabolic reflector, near the focus of which the tubes were placed, either naked or surrounded by a solution of sulphate of copper to absorb the calorific rays. By this arrangement the light and heat could be increased, diminished or modified at pleasure, which was found very convenient in several of the operations.

Action of Tin upon Iodide of Ethyl.

When iodide of ethyl and metallic tin are exposed to the action of either heat or light, the tin gradually dissolves in the ethereal liquid, which finally solidifies to a mass of nearly colourless crystals. This reaction is effected most conveniently by the action of light, an excess of tinfoil, cut into narrow slips, being employed: the sealed tubes containing these ingredients should be placed near the focus of a large parabolic reflector, the temperature being prevented, if necessary, from rising too high by immersing them in water or in a solution of sulphate of copper. The unconcentrated rays of the sun, or even diffused daylight, are quite sufficient to determine the formation of the crystalline body; but an exposure of several weeks, or even months, would be necessary for the completion of the change, which is effected by the use of the reflector in a few days of bright sunshine. The liquid gradually assumes a straw-yellow colour, but its solidification is prevented as long as possible at the end of the operation, by allowing the temperature to rise 20° or 30° C. above that of the atmosphere; thus nearly the whole of the iodide of ethyl becomes united with tin. When heat instead of light is employed to effect the combination, the tubes should not be more than half an inch in diameter, and to avoid the risk of explosion, should not be more than one-fourth filled with the materials: the combination takes place at about 180° C. The agency of heat is therefore much less convenient than that of light in the production of this reaction, which is also never so complete as when the latter agent is employed; I have satisfied myself, however, that the results are the same in both cases.

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* A minute account of the construction and use of these tubes is given in the Journal of the Chemical Society, vol. ii. p. 265.

Examination of Solid Products.

The capillary extremities of the tubes in which the iodide of ethyl had been exposed to the action of tin, were broken off under sulphuretted water and beneath a jar filled with the same liquid*; the gases evolved were preserved for eudiometrical investigation. The crystalline product of the reaction was then withdrawn from the tubes, and after being exposed to a gentle heat for a few minutes to expel the iodide of ethyl that had escaped combination, was treated with alcohol, in which the crystals readily dissolved, leaving only a small residue of a bright red colour, which proved to be protoiodide of tin. The filtered alcoholic solution was then placed over sulphuric acid *in vacuo*, where it soon deposited a large crop of long needle-like crystals, which, when freed from the mother-liquor, washed with a small quantity of dilute alcohol, dried between folds of bibulous paper, and finally over sulphuric acid *in vacuo*, yielded the following analytical results :—

I. 1·6806 grm., treated with aqueous solution of ammonia, was immediately decomposed, iodide of ammonium being formed, whilst the iodine in the original compound became, as I shall show below, replaced by oxygen; this oxide, which is almost absolutely insoluble in ammonia, collected on a filter and dried at 100° C., weighed ·7263 grm.; decomposed by boiling nitric acid it gave ·5811 grm. peroxide of tin. The ammoniacal solution, acidulated with nitric acid and precipitated by nitrate of silver, yielded 1·8418 grm. iodide of silver. After precipitation of the excess of nitrate of silver by hydrochloric acid, sulphuretted hydrogen was passed through the solution, and the slight precipitate formed was washed, dried, ignited and added to the above peroxide of tin, in the weight of which it is included.

II. 1·4254 grm., burnt with oxide of copper, 2 inches of metallic copper being placed in front of the combustion-tube, gave ·5858 grm. carbonic acid and ·2975 grm. water.

III. 1·2209 grm. gave 0·5008 grm. carbonic acid and ·2580 grm. water.

IV. 2·0980 grms., treated as described in No. I., yielded ·9218 grm. of the body produced by the action of solution of ammonia, which yielded ·7239 grm. peroxide of tin. The ammoniacal solution, precipitated by nitrate of silver as in No. I., produced 2·2883 grms. iodide of silver.

V. ·9113 grm. gave ·3735 grm. carbonic acid and ·1908 grm. water†.

These numbers show that the crystalline body is a compound of one atom of ethyl, one atom of tin, and one atom of iodine. The formula—

$$C_4 H_5 Sn I$$

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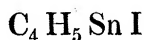
* Journal of Chemical Society, vol. ii. p. 267.

† The substance used in Nos. IV. and V. was produced by the action of light, that used in the other analyses by the agency of heat.

requires the following values :—

	Calculated.		I.	II.	III.	IV.	V.
				Found.			
C_4	24	11·18	——	11·21	11·19	——	11·18
H_5	5	2·33	——	2·32	2·35	——	2·33
Sn	58·82	27·40	27·18	——	——	27·12	
I	126·84	59·09	59·21	——	——	58·76	
		100·00					

For reasons described below, I propose to call this compound *iodide of stanethylium*.

Iodide of stanethylium crystallizes in transparent, slightly straw-coloured needles, which are right rectangular prisms, frequently one-twelfth of an inch broad and 2 or 3 inches in length. They are very soluble in ether and in boiling alcohol; less so in cold alcohol and in water; the watery solution is decomposed on boiling, oxide of stanethylium being precipitated and hydriodic acid formed. Iodide of stanethylium fuses at 42° C., and boils at 240° C., undergoing at the same time partial decomposition: it possesses, at common temperatures, a peculiar pungent odour, somewhat resembling the volatile oil of mustard, and which irritates the eyes and lining membrane of the nose, causing a discharge which continues for several hours or even days, especially if the vapour from the heated iodide of stanethylium be inhaled; yet this compound can scarcely be said to be volatile at common temperatures, since a few grains may be exposed to the air for several weeks without any appreciable loss of weight.
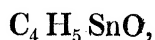
Oxide of Stanethylium.

In contact with solutions of the alkalies, iodide of stanethylium is immediately decomposed, oxide of stanethylium and an alkaline iodide being formed; with solutions of potash and soda the oxide of stanethylium dissolves in an excess of the precipitant, but is reprecipitated, unchanged, by cautious neutralization of the alkaline solution; with solution of ammonia the precipitated oxide remains undissolved on the addition of an excess of the alkali; a quantity of the oxide of stanethylium, prepared in this latter manner, was heated for a few minutes with an excess of ammonia, thrown on a filter and washed with distilled water until all iodide of ammonium was removed. Submitted to analysis it yielded the following results :—

I. ·3497 grm., burnt with oxide of copper, gave ·3218 grm. carbonic acid and 1630 grm. water.

II. ·7296 grm., decomposed by nitric acid and ignited, gave ·5778 grm. peroxide of tin.

III. ·9218 grm. gave, when similarly treated, ·7239 grm. peroxide of tin.

These numbers agree closely with the formula—

$$C_4 H_5 SnO,$$

as is seen by the following comparison :—

	Calculated.		Found.		
			I.	II.	III.
C_4	24	25·05	25·09	——	——
H_5	5	5·22	5·18	——	——
Sn	58·82	61·39	——	62·25	61·73
O	8	8·34	——	——	——
		100·00			

Analyses Nos. I. and IV. of iodide of stanethylium also clearly show the transformation of the iodide into the oxide of stanethylium by ammonia; in analysis No. I. 1·6806 grm. of iodide of stanethylium gave ·7263 grm. of oxide of stanethylium, and in analysis No. IV. 2·0980 grms. of the iodide yielded ·9218 grm. of the oxide of stanethylium. Hence

	Calculated.	Found.	
		I.	II.
100 parts of iodide of stanethylium yield of oxide of stanethylium	44·64	43·22	43·93

The numbers obtained by experiment correspond sufficiently well with the theoretical one, when it is considered that oxide of stanethylium is not absolutely insoluble in excess of ammonia.
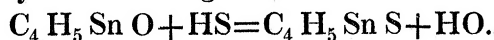
Oxide of stanethylium presents the appearance of a somewhat cream-white amorphous powder, closely resembling peroxide of tin, but less heavy than that oxide; it has a peculiar though slight ethereal odour and a bitter taste; it is insoluble in water, alcohol and ether, but readily dissolves in solutions of acids and of the fixed alkalies; with acids it forms salts, which are, however, for the most part difficultly crystallizable; those with strong acids exhibit an acid reaction. The nitrate deflagrates when heated to about 120° C., and on the application of a higher heat becomes pure peroxide of tin. The salts of oxide of stanethylium behave with reagents so nearly like the salts of peroxide of tin, that the two are very difficult to distinguish from each other.

Sulphide of Stanethylium.

When sulphuretted hydrogen is passed through an acid solution of a salt of stanethylium, a cream-coloured precipitate falls, which is insoluble in dilute acids and ammonia, but soluble in concentrated hydrochloric acid, solutions of the fixed alkalies, and alkaline sulphides; from its solutions in the fixed alkalies and alkaline sulphides, it is reprecipitated, unchanged, on the addition of an acid. I have made no analyses of this body, but there is no doubt that its formula is—

$$C_4 H_5 Sn S,$$
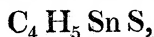
and that it is produced by the following reaction—

$$C_4 H_5 Sn O + HS = C_4 H_5 Sn S + HO.$$

Sulphide of stanethylium presents the appearance of an amorphous cream-coloured

powder, having a pungent and very nauseous smell, resembling decayed horse-radish: when heated it fuses, froths up and decomposes, emitting vapours of a most insupportable odour. Heated with nitric acid it is decomposed with the formation of peroxide of tin.

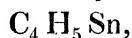### Chloride of Stanethylium.

$$C_4 H_5 Sn Cl.$$

This salt is best prepared by dissolving oxide of stanethylium in dilute hydrochloric acid: on evaporation at a gentle heat or over sulphuric acid *in vacuo*, the chloride crystallizes out in long colourless needles, isomorphous with the iodide, which salt it also closely resembles in all its properties; it is however more volatile, and therefore emits a more intensely pungent and irritating odour than the iodide.

Stanethylium.

When a strip of zinc is immersed in a solution of a salt of stanethylium (a solution of the chloride of stanethylium is the best for this purpose), it speedily becomes covered with dense oily drops of a yellow colour, which finally separate from the lower extremity of the zinc and accumulate at the bottom of the vessel; the formation of the oily liquid is much favoured by the application of a gentle heat. The yellow oil was separated from the supernatant liquid by means of a pipette, and well washed with successive large portions of cold water; being then dried over chloride of calcium and submitted to analysis, it yielded the following results:—

I. ·3150 grm., burnt with oxide of copper and oxygen gas, gave ·3498 grm. carbonic acid and ·1757 grm. water.

These numbers correspond sufficiently with the formula

$$C_4 H_5 Sn,$$

when it is considered that the stanethylium, as thus prepared, contains traces of undecomposed chloride of stanethylium, which I did not succeed in removing by the most protracted washing; and as stanethylium does not crystallize and cannot be distilled without decomposition, I could not avail myself of these means of purification. The above formula requires the following numbers:—

								Calculated.	Found.
C_4	.	.	.	.	.	.	24	27·32	26·95
H_5	.	.	.	.	.	.	5	5·69	5·51
Sn	.	.	.	.	.	.	58·82	66·99	———
								100·00	

The isolation of stanethylium from its chloride by zinc, is therefore expressed by the following simple equation:—

$$\left.\begin{array}{l} C_4 H_5 Sn Cl \\ Zn \end{array}\right\} = \left\{\begin{array}{l} Zn Cl \\ C_4 H_5 Sn. \end{array}\right.$$
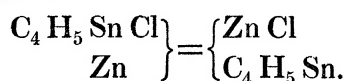
Stanethylium exists at the ordinary atmospheric temperature, as a thick, heavy, oily liquid, of a yellow or brownish-yellow colour, and an exceedingly pungent odour, resembling that of its compounds, but much more powerful. It is insoluble in water,

but soluble in alcohol and ether. At about 150° C. it enters into ebullition, a quantity of metallic tin is deposited, and a colourless liquid distils over, having a peculiar odour, containing a considerable quantity of tin, and exhibiting no tendency to combine with iodine or bromine: the composition and properties of this liquid I have not further ascertained; it possibly consists of or contains *binethide of tin* ($Sn (C_4 H_5)_2$). In contact with the air stanethylium rapidly attracts oxygen and is converted into a white powder, which has all the properties of oxide of stanethylium. Chloride, bromide and iodide of stanethylium are immediately formed by the action of chlorine, bromine and iodine, or their hydrogen acids respectively, upon stanethylium; the first and third are in every respect identical with the salts above described. I have analytically examined the bromide prepared by adding an alcoholic solution of bromine to an alcoholic solution of stanethylium until the colour of the bromine no longer disappears; by spontaneous evaporation the bromide of stanethylium is deposited in long white needles, which closely resemble, both in appearance and properties, the chloride of stanethylium. These crystals, pressed between folds of bibulous paper, and dried over sulphuric acid *in vacuo*, gave the following analytical results:—

·9730 grm., burnt with oxide of copper, yielded ·5108 grm. carbonic acid and ·2582 grm. water.

These numbers agree very closely with the formula—

$$C_4 H_5 Sn Br,$$

as is seen from the following comparison:—

	Equivs.		Calculated.	Found.
Carbon	4	24	14·30	14·32
Hydrogen	5	5	2·98	2·95
Tin	1	58·82	35·05	——
Bromine	1	80·00	47·67	——
		167·82	100·00	

These results show that stanethylium perfectly resembles cacodyl in its reactions, combining directly with the electro-negative elements and regenerating the compounds from which it has been derived.

Examination of Gases.

The examination of the gases evolved on opening the tubes in which iodide of ethyl and tin had been submitted to the action of heat, and which were allowed to stand over sulphuretted water for twelve hours, yielded the following results. Specific gravity:—

Weight of flask filled with gas	35·4712 grms.
Temperature of room	20·8° C.
Height of barometer	761·2 mm.
Height of internal column of mercury . .	15·2 mm.
Temperature in balance case	22°·6 C.

Weight of flask filled with dry air   . . .   35·4703 grms.

Temperature in balance case . . . . .   22·8° C.

Capacity of flask . . . .   140·50 cubic centimetres.

From these data the specific gravity was calculated to be 1·0384.

The remainder of the gas was submitted to eudiometrical analysis: the following numbers were obtained:—

I. In Short Eudiometer.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol. at 0° C. and 1 metre press.
			mm	mm	
Volume of gas used (dry)	143·4	21·0 C.	16·3	760·5	99·09
Volume after action of fuming SO_3 (dry) .	122·5	18·2	37·0	754·7	82·42

II. In Combustion Eudiometer.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol.
Volume of gas used (moist)	110·3	18·1 C.	570·7	755·2	17·48
Volume after admission of O (moist)	383·6	18·3	274·7	755·7	167·31
Volume after explosion (moist)	326·9	18·4	332·4	755·8	124·86
Volume after absorption of CO_2 (dry) . . .	264·5	17·0	398·3	760·7	90·23
Volume after admission of H (dry)	592·5	17·0	77·9	761·6	381·33
Volume after explosion (moist)	303·5	17·7	355·9	762·7	111·64

As the gas, left unabsorbed by fuming sulphuric acid, was soluble in about its own volume of alcohol, with the exception of a very small per-centage due to the nitrogen introduced by diffusion through the sulphuretted water, it could not contain either hydrogen or hydride of methyl; and the result of the above combustion proves that it is hydride of ethyl, for I have shown that 1 vol. of hydride of ethyl consumes 3·5 vols. oxygen, and generates 2 vols. carbonic acid, numbers which almost exactly correspond with those obtained.

17·48 vols. of the gas, containing 17·15 vols. of combustible gas and ·33 vol. of nitrogen, consumed 59·93 vols. oxygen and generated 34·63 vols. carbonic acid; hence

Volume of combustible gas.		Oxygen consumed.		Carbonic acid generated.
17·15		59·93		34·63
1	:	3·49	:	2·01

Further, the gas agrees in all its chemical and physical properties, with the hydride of ethyl prepared by the action of zinc upon iodide of ethyl in presence of water.

The composition of the gas absorbed by fuming sulphuric acid was determined

by exploding a known volume of the original gas with excess of oxygen, and determining the quantities of oxygen consumed, and carbonic acid generated.

This determination gave the following numbers:—

III.

	Observed volume.	Temp.	Difference of mercury level. mm	Barom. mm	Corrected vol. at 0° C. and 1 metre press.
Volume of gas used (moist)	122·0	19·7 C.	563·0	764·2	20·95
Volume after admission of O (moist)	424·5	20·0	240·4	764·3	200·33
Volume after explosion (moist)	363·5	20·4	301·0	763·5	150·40
Volume after absorption of CO_2 (dry) . . .	296·7	19·7	366·4	760·4	109·03
Volume after admission of H (dry)	683·1	21·7	4·0	760·8	478·89
Volume after explosion (moist)	368·6	21·8	293·3	761·2	153·09

Hence 20·95 vols. containing 20·62 vols. combustible gas, consumed 70·78 vols. oxygen, and generated 41·37 vols. carbonic acid: now as 20·62 vols. of this gas must contain, according to analyses Nos. I. and II., 17·10 vols. hydride of ethyl, which would consume 59·85 vols. oxygen and generate 34·20 vols. carbonic acid, it is evident that the volumes of oxygen consumed, and carbonic acid generated, by the gas absorbed by fuming sulphuric acid, must bear the following relation to each other:—

Volume of gas absorbable by fuming SO_3.		Oxygen consumed.		Carbonic acid generated.
3·52		10·93		7·17
1	:	3·10	:	2·03

The body removed by fuming sulphuric acid is therefore olefiant gas, 1 vol. of which consumes 3 vols. oxygen, and generates 2 vols. carbonic acid, numbers which correspond sufficiently with those obtained in the above determination.

The last analysis can also be employed to control Nos. I. and II.; for if we represent the volume of nitrogen, contained in the original gas, by x, that of hydride of ethyl by y, and that of olefiant gas by z; and further, the volume of mixed gases, oxygen consumed, and carbonic acid generated, respectively by A, B and C, we have the following equations:—

$$x + y + z = A$$

$$\frac{7}{2}y + 3z = B$$

$$2y + 2z = C,$$

from which the following values for x, y and z are derived :—

$$x= \cdot 27$$
$$y=17\cdot 06$$
$$z= 3\cdot 62$$
$$\overline{20\cdot 95}$$

The per-centage composition of the gases evolved by the action of heat upon iodide of ethyl and tin is therefore the following :—
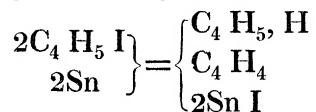
	I. and II.	III.
Hydride of ethyl	81·61	81·43
Olefiant gas	16·82	17·28
Nitrogen	1·57	1·29
	100·00	100·00

This result is also confirmed by the determination of the specific gravity of the gaseous mixture, as is seen from the following calculation :—

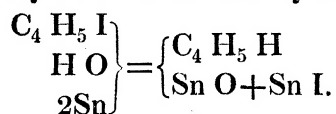|		
$C_4 H_5 H$	$81\cdot 61 \times 1\cdot 03652 = 84\cdot 590$	
$C_4 H_4$	$16\cdot 82 \times \cdot 96742 = 16\cdot 272$	
N	$1\cdot 57 \times \cdot 96740 = 1\cdot 519$	
	100·00	102·381

$$\frac{102\cdot 381}{100} = 1\cdot 02381$$

Specific gravity found by experiment . . . . . . $= 1\cdot 0384$

The presence of hydride of ethyl and olefiant gas amongst the products of the action of heat upon iodide of ethyl and tin, shows that the combination of tin with iodide of ethyl is not the only reaction which takes place, but that a portion of the iodide of ethyl is also decomposed by the tin, with the production of iodide of tin and ethyl; the latter body being transformed at the moment of its liberation into hydride of ethyl and olefiant gas, a catalysis to which this radical is so prone,

$$\left. \begin{array}{c} 2C_4 H_5 I \\ 2Sn \end{array} \right\} = \left\{ \begin{array}{l} C_4 H_5, H \\ C_4 H_4 \\ 2Sn I \end{array} \right.$$

It was ascertained that protoiodide of tin was present amongst the solid products of the reaction.

The large excess of hydride of ethyl exhibited in the above analysis, may have been caused, either by the greater solubility of olefiant gas in iodide of ethyl (a further and considerable amount of gas being expelled from the tube by the application of a gentle heat), or by the presence of moisture in the materials, which would give rise to the formation of oxyiodide of tin and hydride of ethyl,

$$\left. \begin{array}{c} C_4 H_5 I \\ H O \\ 2Sn \end{array} \right\} = \left\{ \begin{array}{l} C_4 H_5 H \\ Sn O + Sn I. \end{array} \right.$$

Both these causes probably contribute to produce the excess of hydride of ethyl; but the very small amount of gaseous products, compared with the solid ones, convinced me that the production of the former is only an accidental circumstance, which, however it may be interpreted, does not at all affect the principal reaction, viz. the formation of iodide of stanethylium. The gases, evolved by the action of light upon iodide of ethyl and tin, are perfectly similar to those obtained by the action of heat.

Stanmethylium and stanamylium are formed when the iodides of methyl and amyl respectively are exposed to the action of light in contact with tin; their salts are isomorphous with those of stanethylium; but I have not yet completed the investigation of these bodies.

Action of Zinc upon Iodide of Methyl.

When iodide of methyl and zinc are exposed to a temperature of about 150° C. in a sealed tube, the zinc gradually dissolves with the evolution of gas, whilst a mass of white crystals and a colourless mobile liquid, refracting light strongly, occupy, after a few hours, the place of the original materials. The gas, evolved on breaking off the capillary extremity of the previously exhausted decomposition tube, was collected and preserved over sulphuretted water in the manner already described: I will refer to this gas again under the name of α. On cutting off the upper portion of the decomposition tube and pouring cold distilled water upon the mobile liquid and white mass of crystals just mentioned, a very violent action ensued, and a column of flame several feet high shot up momentarily from the mouth of the tube; but the action soon became more moderate, and a cork and gas-delivering tube being fitted into the decomposition tube, the gas, after all atmospheric air had been expelled, was collected and preserved in an apparatus similar to that used for the gas α. I will call this second gas β.

Zincmethylium.

From a preliminary experiment, it was ascertained that the gas evolved on opening the decomposition tube possessed, before contact with water, a most insupportable and very peculiar odour, and that, when ignited or brought in contact with pure oxygen gas, it burnt with a greenish blue flame, producing dense white fumes: when a porcelain plate was held in this flame, it immediately became coated with a jet black deposit, surrounded by a white ring; this black deposit dissolved in dilute hydrochloric acid with evolution of hydrogen gas, and the solution was found to contain chloride of zinc. Hence it was evident that a volatile or gaseous compound of zinc was present amongst the products of decomposition, and this was soon found to reside in the mobile liquid above mentioned; for on inverting the tube and allowing a few drops of the liquid to escape, it inflamed spontaneously the instant it came in contact with the air, and produced, by its combustion, large quantities of oxide of

zinc. In order to obtain this liquid in a state of purity, another tube was charged with iodide of methyl and excess of zinc, and subjected to a heat of 150° or 160° C. until every trace of iodide of methyl was decomposed. The drawn out extremity of the tube being broken off, the included gas was allowed to escape, and the liquid contents were then separated from the solid ones by distillation at a gentle heat, in an atmosphere of dry hydrogen. This was accomplished as shown in the following figure.
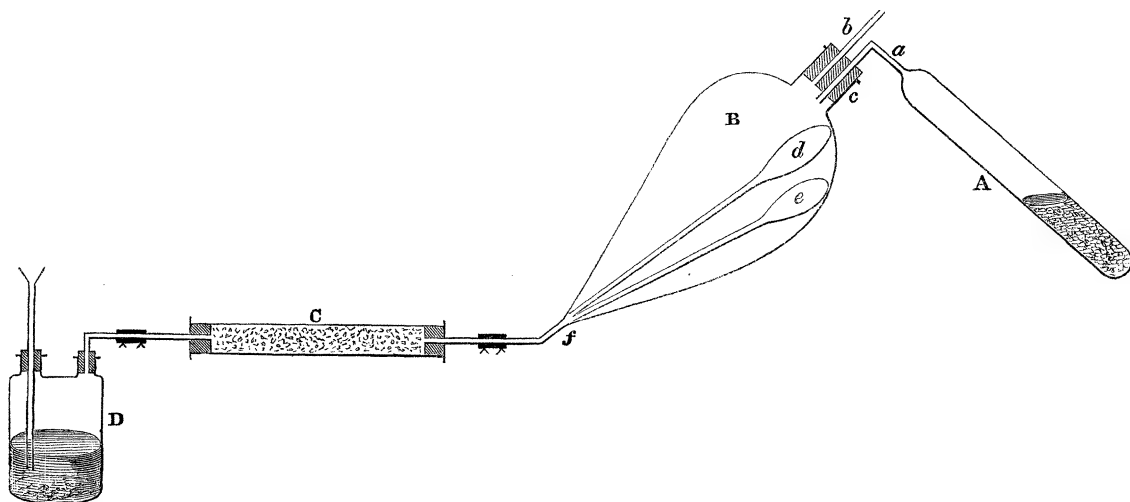
A is the decomposition tube bent at an obtuse angle at a, and connected with the receiver B by the doubly perforated cork c, which also contains the small tube b, open at both ends. The receiver B is drawn out at f until its internal diameter is diminished to about $\frac{1}{20}$th of an inch, and this drawn out extremity is connected, by means of a caoutchouc joint, with the chloride of calcium tube C, which at its opposite extremity is in connection with a hydrogen gas apparatus D. d, e are two small glass bulbs for preserving the condensed liquid. The apparatus being thus arranged, hydrogen is evolved in D, and becoming perfectly desiccated in passing through the chloride of calcium tube C, enters the receiver B at f, expelling the atmospheric air through the tube b. When the gas has thus streamed through the apparatus for at least a quarter of an hour, and every trace of air has been expelled from B and from the bulbs d, e by diffusion, the extremity of the tube b is hermetically sealed, at the same moment that the evolution of gas from D is interrupted. The drawn out extremity of the receiver B being then quickly sealed at f; B, d and e remain filled with pure dry hydrogen, and A with a mixture of gases free from oxygen, as any trace of this element, which might have penetrated there, would be instantaneously absorbed by its contents. B is then immersed to its neck in cold water, and a gentle heat cautiously applied to the whole length of A by means of a spirit lamp. The mobile fluid in A soon enters into ebullition, and distils over into the receiver B; as soon as the distillation is finished and A become cold, its capillary ex tremity is fused off at a by means of a blowpipe, a remaining hermetically sealed.

The receiver B is then removed from the water and dried; heat is applied to the side adjacent to the bulbs *d, e,* so as to expel a portion of the enclosed gas from their open ends at *f*; on subsequent cooling, a certain quantity of the liquid rises into these bulbs, which are alternately heated and cooled, until every trace of the liquid has not only entered them but passed entirely into their expanded portion, so as to leave the capillary limbs filled with hydrogen. It is of importance that the whole of the liquid should be forced to enter these bulbs, otherwise, on subsequently opening the mouth of the receiver, it inflames, causing the expulsion of the liquid from the bulbs, and thus rendering the experiment abortive. The cork *c* is then removed, and the bulbs *d, e* extracted as quickly as possible, the open capillary extremities being immediately sealed before the blowpipe. The bulbs, having been previously weighed, the increase denotes the weight of the included liquid. The residue in A was found scarcely to effervesce with water, and consisted of iodide of zinc mixed with the excess of metallic zinc employed.

I have fixed the composition of the liquid obtained as above described, and proved it to be a compound of one atom of zinc and one atom of methyl, by the following experiments:—

I. One of the bulbs above mentioned was opened beneath an inverted receiver filled with recently boiled distilled water; its contents were rapidly resolved into hydrated oxide of zinc and a permanent gas, which last was submitted to eudiometrical examination; the following results were obtained:—

The action of fuming sulphuric acid did not produce any diminution of volume.

The gas was nearly insoluble in absolute alcohol.

A eudiometrical combustion yielded the following results:—

	Observed volume.	Temp.	Difference of mercury level. mm	Barom. mm	Corrected vol. at 0° C. and 1 metre press.
Volume of gas used (moist)	122·5	18·7 C.	602·2	747·8	14·86
Volume after admission of O (moist)	287·9	18·7	418·4	747·6	84·39
Volume after explosion (moist)	232·1	18·6	479·7	747·4	54·71
Volume after absorption of CO_2 (dry) . . .	188·2	18·6	519·4	747·5	40·19
Volume after admission of H (dry)	549·4	18·4	162·7	747·6	301·04
Volume after explosion (moist)	425·7	18·4	279·0	747·6	180·62

Volume of comb. gas.	Oxygen consumed.	CO_2 generated.
14·86	29·39	14·52
1 :	1·98 :	·98

In order to ascertain whether the gas was a single compound or a gaseous mix-

ture, and also to determine its specific gravity, it was submitted to diffusion in an apparatus which I have already described*: the following results were obtained :—

I. In Diffusion Eudiometer.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol. at 0° C. and 1 metre press.
			mm	mm	
Volume of gas used (dry)	173·0	19·0 C.	20·1	741·1	116·61
Volume after diffusion (dry)	144·3	19·2	46·3	740·8	93·63

II. Estimation of Oxygen in residual gas.

Volume of gas used (moist)	117·5	19·3	53·1	740·6	75·44
Volume after absorption of O (dry)	101·2	17·0	69·3	742·8	64·16

III. Combustion of Gas remaining after absorption of Oxygen.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol. at 0°C. and 1 metre press.
			mm	mm	
Volume of gas used (moist)	155·9	17·3 C.	558·7	743·3	24·91
Volume after admission of O (moist)	302·7	17·7	399·0	744·0	93·78
Volume after explosion (moist)	270·2	17·6	433·2	744·2	75·13
Volume after absorption of CO_2 (dry)	246·3	17·8	458·7	744·7	66·13
Volume after admission of H (dry)	522·3	17·9	182·4	745·1	275·80
Volume after explosion (moist)	349·5	18·0	350·5	745·0	124·30

The gas, remaining after diffusion and subsequent absorption of oxygen, therefore contained in 24·91 vols. 15·63 vols. nitrogen and 9·28 vols. combustible gas, which last was a single gas and not a mixture, since it consumed the same amount of oxygen and generated the same amount of carbonic acid after as before diffusion :—

Volume of combustible gas.	Oxygen consumed.	CO_2 generated.
9·28	18·37	9·00
1 :	1·98 :	·97

Experiments Nos. I., II. and III., taken together, enable us to ascertain the volume of the gas which escaped and that of the air which entered during the diffusion experiment; these volumes are as follow :—

Volume of gas escaped . . . . 86·95

Volume of air entered . . . . 63·97

* Quarterly Journal of Chemical Society, vol. ii. p. 283.

Hence, according to the well-known law of diffusion, the specific gravity of the gas must be ·5413.

The gas is therefore hydride of methyl (light carburetted hydrogen), 1 vol. of which consumes 2 vols. oxygen and generates 1 vol. carbonic acid, and the specific gravity of which is ·5528, numbers which correspond almost exactly with those obtained by experiment.

II. A glass jar, graduated in cubic centimetres, was filled with recently boiled distilled water, to which about twenty drops of sulphuric acid had been added, and inverted in a shallow glass dish containing the same liquid; the other bulb was then introduced into the inverted jar, and its capillary extremity broken off against the side of the vessel; the water now slowly gained access to the liquid in the bulb and steady decomposition ensued, the oxide of zinc dissolving as fast as formed, in the dilute sulphuric acid, and the hydride of methyl collecting in the inverted jar. When the decomposition was quite complete, the volume of gas was read off with the usual corrections for temperature and pressure, the graduated jar rinsed out and removed, and the solution of sulphate of zinc in the glass dish, after being evaporated to a smaller bulk, was treated with carbonate of potash and the zinc precipitated as basic carbonate, and weighed as oxide with the usual precautions: the following results were obtained:—

·3109 grm. gave ·2660 grm. oxide of zinc, and 138·15 cubic centimetres dry hydride of methyl, at 0° C. and 760 mm. pressure, equivalent to ·0930 grm.

These numbers agree sufficiently with those calculated from the formula

$$C_2 H_3 Zn,$$
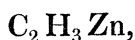
when we consider that every trace of oxygen, which gained admission to the ethereal fluid before its decomposition, would diminish the volume of hydride of methyl, which would also be liable to further diminution, from the solvent action of the fluid over which it was determined:—

	Calculated.		Found.
1 equiv. of Methyl	15	31·56	29·91
1 equiv. of Zinc	32·52	68·44	68·67
	47·52	100·00	98·58

This compound, for which I propose the name Zincmethylium, possesses the following properties:—It is a colourless, transparent and very mobile liquid, refracting light strongly, and possessing a peculiar penetrating and insupportable odour; it is very volatile, but I have not yet been able to determine its boiling-point with accuracy.

Zincmethylium combines directly with oxygen, chlorine, iodine, &c., forming somewhat unstable compounds, a description of which I reserve for a future communication. Its affinity for oxygen is even more intense than that of potassium; in contact with atmospheric air it instantaneously ignites, burning with a beautiful greenish-blue flame, and forming white clouds of oxide of zinc; in contact with pure oxygen it

burns with explosion, and the presence of a small quantity of its vapour in combustible gases gives them the property of spontaneous inflammability in oxygen. Thrown into water, zincmethylium decomposes that liquid with explosive violence and with the evolution of heat and light; when this action is moderated, so as to prevent any great rise of temperature, the sole products of the decomposition are oxide of zinc and hydride of methyl,

$$\left.\begin{array}{c} C_2 H_3 Zn \\ HO \end{array}\right\} = \left\{\begin{array}{c} C_2 H_3 H \\ Zn O. \end{array}\right.$$
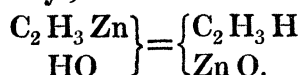
The extraordinary affinity of zincmethylium for oxygen, its peculiar composition, and the facility with which it can be procured, cannot fail to cause its employment for a great variety of transformations in organic compounds; by its agency there is every probability that we shall be able to replace oxygen, chlorine, &c., atom for atom, by methyl, and thus produce entirely new series of organic compounds, and obtain clearer views of the rational constitution of others. I intend to pursue this branch of the subject whilst studying the compounds of zincmethylium and the corresponding bodies containing ethyl and amyl.

Examination of the Gas α.

A quantity of this gas, after standing over sulphuretted water until all traces of iodide of methyl vapour had been absorbed, was transferred into a suitable flask for the determination of its specific gravity; the following numbers were obtained:—

Temperature of room . . . . $18°\cdot6$ C.

Height of barometer . . . . $754\cdot2$ mm.

Height of inner column of mercury . . . $15\cdot2$ mm.

Weight of flask and gas . . . . $35\cdot4161$ grms.

Temperature in balance case . . . . . . $19°\cdot6$ C.

Weight of flask and dry air . . . . . . $35\cdot4500$ grms.

Temperature in balance case . . . . . . $20°\cdot2$ C.

Capacity of flask . . . . $140\cdot51$ cubic centimetres.

From these data the specific gravity was calculated to be $\cdot79598$.

The eudiometrical analysis of the gas gave the following results:—

I. In Short Eudiometer.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol. at 0°C. and 1 metre press.
			mm	mm	
Volume of gas used (dry)	194·7	18·6C.	2·1	754·2	137·06
Volume after action of fuming SO_3 (dry). . .	194·8	18·7	2·2	753·5	137·03
Volume after removal of specimen for combustion (dry)	153·8	19·0	22·0	741·0	103·38
Volume after action of alcohol	82·0	18·7	7·0	741·4	53·72

II. In Combustion Eudiometer.

	Observed volume.	Temp.	Difference of mercury level. mm	Barom. mm	Corrected vol. at 0°C. and 1 metre press.
Volume of gas used (moist)	101·5	18·9 C.	621·7	752·4	10·86
Volume after admission of O (moist)	388·1	18·6	311·7	752·0	154·20
Volume after explosion (moist)	354·6	18·5	345·8	752·2	129·71
Volume after absorption of CO_2 (dry)	321·1	18·3	376·9	752·0	112·88
Volume after admission of H (dry)	745·1	18·7	·8	751·1	523·19
Volume after explosion (moist)	428·3	18·7	274·1	750·5	184·54

III.

	Observed volume.	Temp.	Difference of mercury level. mm	Barom. mm	Corrected vol. at 0° C. and 1 metre press.
Volume of gas used (moist)	104·2	18·8 C.	619·2	750·5	11·23
Volume after admission of O (moist)	371·2	18·9	330·6	750·2	140·04
Volume after explosion (moist)	335·0	18·9	367·7	750·2	114·76
Volume after absorption CO_2 (dry)	299·0	18·2	401·3	750·3	97·83
Volume after admission of H (dry)	707·0	18·4	26·9	750·6	479·33
Volume after explosion (moist)	431·6	18·7	273·4	749·8	185·96

Analysis No. I. proves the absence of all the members of the olefiant gas family, and also that the mixture consists of—

Gas absorbable by alcohol . . . . 48·04
Gas unabsorbable by alcohol . . . . 51·96
———
100·00

The behaviour of the iodides of ethyl and amyl in contact with zinc*, led me to expect that the gaseous products of the decomposition of iodide of methyl by the same metal would consist of methyl, hydride of methyl, and the first member of the olefiant gas series, methylene; but in addition to the proof of the absence of this latter body afforded by the absence of all absorption by fuming sulphuric acid, analyses Nos. II. and III. demonstrate the impossibility of methylene being a constituent of the gaseous mixture; for on constructing three equations in which the volumes of

* Journal of the Chemical Society, vol. ii. p. 265, and vol. iii. p. 30.

methyl, hydride of methyl, and methylene are expressed, the value obtained for the last gas is invariably a small negative quantity. The volumes of methyl and hydride of methyl are readily found by the two following equations, in which the volume of combustible gas is represented by A, the contraction produced by explosion with excess of oxygen by B, and the volumes of methyl and hydride of methyl respectively, by x and y, the contraction produced by the explosion of methyl with excess of oxygen being 2·5 times its own volume, and that produced by the explosion of hydride of methyl twice its own volume:—

$$x + y = A,$$

$$\frac{5}{2}x + 2y = B.$$

The values of x and y may therefore be thus expressed:—

$$x = 2B - 4A,$$

$$y = 5A - 2B.$$

According to analysis No. II., 10·88 vols. of combustible gas produced a contraction, on explosion with oxygen, equal to 24·49 vols.; and in analysis No. III., 11·23 vols. of combustible gas produced a contraction, on explosion, equal to 25·28 vols. Hence, by the application of the foregoing equations, the per-centage composition of the gaseous mixture may be expressed as follows:—

	II.	III.	Mean.
Methyl	50·18	50·22	50·20
Hydride of Methyl . . .	49·82	49·78	49·80
	100·00	100·00	100·00

This result is confirmed by the action of alcohol in analysis No. I., and also by the determination of the specific gravity of the mixed gases, which agrees very closely with that deduced from the above numbers, as is seen from the following comparison:—

Methyl	$50·20 \times 1·0365 = 52·0323$
Hydride of Methyl . . .	$49·80 \times ·5528 = 27·5294$
	100·00

$$\frac{79·5617}{100} = ·795617$$

Specific gravity found by experiment . . . $= ·79598$

The origin of the hydride of methyl in the above gaseous mixture is readily perceived, when the volatility of zincmethylium and the method of collecting the gas are taken into consideration; on opening the decomposition-tube beneath water, a copious effervescence was observed wherever the evolved gas came in contact with water; and as this effervescence was accompanied by the formation of a flocculent precipitate of oxide of zinc, it could only be caused by the presence of the vapour of zincmethylium, which, on coming in contact with water, would be instantaneously decomposed into oxide of zinc and hydride of methyl.

I have not yet endeavoured to procure the methyl free from admixture with hydride

of methyl, but have no doubt that, by collecting the gas as evolved from the decomposition-tube over mercury, and absorbing the zincmethylium vapour by dry iodine, the methyl would be left in a state of purity. It perfectly resembles in its properties, chemical and physical, the methyl procured by KOLBE from the electrolysis of acetic acid *.

Examination of the Gas β.

This gas, evolved by the action of water upon the solid and liquid products of the decomposition of iodide of methyl by zinc, proved, as might have been anticipated, to be pure hydride of methyl, derived from the decomposition of the zincmethylium with which the crystalline residue of iodide of zinc was saturated. Its eudiometrical analysis yielded the following results :—

I. In Short Eudiometer.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol. at 0° C. and 1 metre press.
			mm	mm	
Volume of gas used (dry).	168·9	18·6 C.	3·6	750·2	118·05
Volume after action of fuming SO_3 (dry) . .	169·5	18·7	3·7	749·8	118·35

One volume of absolute alcohol, at 19° C. and 732·6 mm. pressure, absorbed ·175 vol. of this gas.

II. In Combustion Eudiometer.

	Observed volume.	Temp.	Difference of mercury level.	Barom.	Corrected vol. at 0° C. and 1 metre press.
			mm	mm	
Volume of gas used (moist)	126·7	18·9 C.	595·1	744·9	15·83
Volume after admission of O (moist)	344·9	18·9	357·7	744·8	119·64
Volume after explosion (moist)	295·9	18·9	408·7	744·5	88·44
Volume after absorption of CO_2 (dry)	260·7	18·6	446·1	744·3	72·78
Volume after admission of H (dry)	705·7	18·5	24·6	741·3	473·66
Volume after explosion (moist)	513·0	18·6	193·6	741·1	255·35

These results correspond almost exactly with those yielded by hydride of methyl, 1 vol. of which requires 2 vols. of oxygen for combustion, and generates 1 vol. of carbonic acid.

Volume of combustible gas.	Oxygen consumed.	CO_2 generated.
15·83	31·04	15·66
1 :	1·96 :	·99

* Journal of the Chemical Society, vol. ii. p. 173.

By the action of zinc upon iodide of methyl, therefore, two distinct decompositions take place, viz. 1st, the decomposition of iodide of methyl by zinc with the production of iodide of zinc and methyl,

$$\left.\begin{array}{c} C_2 H_3 I \\ Zn \end{array}\right\} = \left\{\begin{array}{l} C_2 H_3 \\ Zn\, I, \end{array}\right.$$
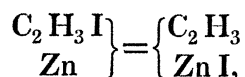
and 2nd, the decomposition of iodide of methyl by zinc, with the formation of iodide of zinc and zincmethylium,

$$\left.\begin{array}{c} C_2 H_3 I \\ 2Zn \end{array}\right\} = \left\{\begin{array}{l} C_2 H_3\, Zn \\ Zn\, I. \end{array}\right.$$
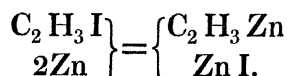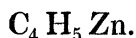
Zincethylium.

This body is formed under precisely the same circumstances as zincmethylium, iodide of ethyl being substituted for iodide of methyl; it is a colourless and transparent liquid, refracting light strongly, and having a peculiar penetrating odour; it is less volatile than zincmethylium, and is not so readily prepared pure, owing to its retention of a small quantity of ethyl gas in solution; its affinities are also somewhat weaker than zincmethylium, and it only takes fire in air spontaneously when exposed in considerable quantity. When allowed to absorb oxygen slowly, it forms a white amorphous oxide; it combines also directly with iodine, chlorine and bromine. In contact with water it is instantaneously decomposed into oxide of zinc and hydride of methyl,
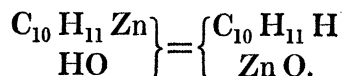
$$\left.\begin{array}{c} C_4 H_5\, Zn \\ HO \end{array}\right\} = \left\{\begin{array}{l} C_4 H_5,\, H \\ ZnO. \end{array}\right.$$
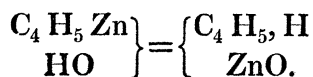
Its formula must therefore be

$$C_4 H_5\, Zn.$$

I reserve for a future communication the complete history of this and the following compound.

Zincamylium.

This body is generated when iodide of amyl is decomposed by zinc at the temperature of 180° C. It is a colourless and transparent liquid which emits white fumes in contact with the air, but does not spontaneously inflame; it is decomposed in contact with water into oxide of zinc and hydride of amyl,

$$\left.\begin{array}{c} C_{10} H_{11}\, Zn \\ HO \end{array}\right\} = \left\{\begin{array}{l} C_{10} H_{11}\, H \\ Zn\, O. \end{array}\right.$$

From this circumstance, and its analogy with zincmethylium, there can be no doubt that its formula is

$$C_{10} H_{11}\, Zn.$$

Action of Mercury upon Iodide of Methyl in presence of Light.

When iodide of methyl is exposed to sunlight in contact with metallic mercury, it

soon becomes coloured red from the separation of free iodine; after several hours' exposure this coloration disappears, and a small quantity of the yellow iodide of mercury subsides to the bottom of the liquid: after the action of sunlight for several days, the bulk of the mercury is observed to have considerably diminished, and white crystals begin to be deposited around the sides of the glass vessel: finally, after about a week's exposure, the liquid solidifies to a colourless crystalline mass: when this is digested with ether, the new compound dissolves, and is thus separated from metallic mercury, and from the small portion of iodide of mercury which is collaterally formed. Only a very small quantity of gas is evolved during the formation of the white crystalline compound. By spontaneous evaporation the ethereal solution solidifies to a mass of minute colourless crystalline scales: these, dried *in vacuo* and submitted to analysis, yielded the following numbers:—

I. ·3170 grm. dissolved in alcohol and treated with nitrate of silver, gave ·2142 grm. iodide of silver.

II. ·6205 grm. burnt with oxide of copper, gave ·0813 grm. carbonic acid, ·0505 grm. water, and ·5960 grm. protoiodide of mercury. The iodide of mercury, a small portion of which was decomposed into metallic mercury and periodide, collected as an incrustation at the front end of the combustion-tube, about a couple of inches of which had been left empty for this purpose, and projected from the furnace, the heat being so regulated that none of the iodide passed into the chloride of calcium tube, whilst none of the watery vapour condensed in the combustion-tube. When the analysis was concluded, the weight of the protoiodide of mercury, mixed with traces of periodide and metallic mercury, was determined by cutting off the part of the combustion-tube containing it, and ascertaining its weight before and after the iodide was removed. The numbers obtained agree very closely with the formula

$$C_2 H_3 Hg I,$$
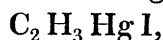
which requires the following values:—

	Calculated.		Found.	
			I.	II.
2 equivs. Carbon . . .	12	3·51	——	3·57
3 equivs. Hydrogen . .	3	·88	——	·90
1 equiv. Mercury . .	200	58·51	——⎫	
1 equiv. Iodine . . .	126·84	37·10	36·56⎬96·05	
	341·84	100·00	100·52	

This compound is therefore evidently the iodide of a new organo-metallic body, consisting of one atom of methyl and one atom of mercury, and for which I propose the name *hydrargyromethylium*: it is formed by the direct union of one atom of mercury with one atom of iodide of methyl, under the influence of light,

$$\left.\begin{matrix} C_2 H_3 I \\ Hg \end{matrix}\right\} = C_2 H_3 Hg I.$$
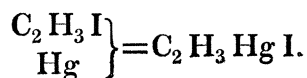
Iodide of hydrargyromethylium is a white solid, crystallizing in minute nacreous scales, which are insoluble in water, moderately soluble in alcohol, and very soluble in ether and iodide of methyl; by the spontaneous evaporation of these solutions the crystals are again deposited unchanged. Iodide of hydrargyromethylium is slightly volatile at ordinary temperatures, and exhales a weak but peculiarly unpleasant odour, which leaves a nauseous taste upon the palate for several days; at 100° C. the volatility is much greater, and the crystals are rapidly dissipated at this temperature when exposed to a current of air. At 143° C. it fuses and sublimes without decomposition, condensing in brilliant and extremely thin crystalline plates. In contact with the fixed alkalies and ammonia, it is converted into oxide of hydrargyromethylium, which is dissolved by excess of all these reagents; from these solutions sulphide of ammonium throws down sulphide of hydrargyromethylium as a slightly yellow flocculent precipitate of a peculiar and most insupportable odour. I have not yet further examined the reactions of this remarkable body, nor have I attempted the isolation of the hydrargyromethylium.

A corresponding compound containing amyl is formed, though with difficulty, under similar circumstances, but I have not yet succeeded in producing one containing ethyl, the iodide of this radical yielding, as I have shown*, when exposed to sunlight in contact with mercury, iodide of mercury, and a mixture of ethyl, hydride of ethyl and olefiant gases.

I have also made some preliminary experiments with other metals, and find that most of them are capable of thus entering into combination with the organic groups, methyl, ethyl, and amyl; amongst those which thus combine under the influence of light most readily, and seem to promise the most interesting results, I may mention arsenic, antimony, chromium, iron, manganese and cadmium. I hope to have the honour of laying before the Royal Society, at an early period, the results of my experiments upon these compounds.

Imperfect as our knowledge of the organo-metallic bodies may yet appear, I am unwilling to close this memoir without directing attention to some peculiarities in the habits of these compounds, which promise at least to throw some light upon their rational constitution, if they do not lead to extensive modifications of our views respecting chemical compounds in general, and especially that interesting class termed conjugate compounds.

That stanethylium, zincmethylium, hydrargyromethylium, &c. are perfectly analogous to cacodyl there can be no reasonable doubt, inasmuch as, like that body, they combine directly with the electro-negative metalloids forming true salts, from which, in most cases, and probably in all, the original group can be again separated unaltered, and therefore any view which may be taken of the new bodies must neces-

* Journal of the Chemical Society, vol. iii. p. 331.

sarily be extended to cacodyl. The discovery and isolation of this so-called organic radical by BUNSEN was certainly one of the most important steps in the development of organic chemistry, and one, the influence of which upon our theoretical views of the constitution of certain classes of organic compounds, can scarcely be too highly estimated. It was impossible to consider the striking features in the behaviour of this body, without finding in them a most remarkable confirmation of the theory of organic radicals, as propounded by BERZELIUS and LIEBIG.

The formation of cacodyl, its habits, and the products of its decomposition, have for some time left no doubt of the existence of methyl ready formed in this body ; and KOLBE*, in developing his views on the so-called conjugate compounds, has proposed to regard it as arsenic conjugated with two atoms of methyl ($(C_2H_3)_2As$). So long as cacodyl was an isolated example of an organo-metallic body, this view of its rational composition, harmonizing as it did so well with the facts elicited during the route of cacodyl through its various combinations and decompositions, could scarcely be contested; but now, since we have become acquainted with the properties and reactions of a considerable number of analogous bodies, circumstances arise, which I consider militate greatly against this view, if they do not render it absolutely untenable. According to the theory of conjugate radicals just alluded to, cacodyl and its congeners, so far as they are at present known, would be thus represented :—

Cacodyl	$(C_2H_3)_2As.$
Oxide of cacodyl	$(C_2H_3)_2AsO.$
Cacodylic acid	$(C_2H_3)_2AsO_3.$
Stanmethylium	$(C_2H_3)Sn.$
Stanethylium	$(C_4H_5)Sn.$
Oxide of stanethylium	$(C_4H_5)SnO.$
Stanamylium	$(C_{10}H_{11})Sn.$
Zincmethylium	$(C_2H_3)Zn.$
Zincethylium	$(C_4H_5)Zn.$
Zincamylium	$(C_{10}H_{11})Zn.$
Stibethine (Stibethyl)	$(C_4H_5)_3Sb.$
Binoxide of stibethine	$(C_4H_5)_3Sb\,O_2.$
Oxide of stibmethylium	$(C_2H_3)_4Sb\,O.$
Hydrargyromethylium	$(C_2H_3)Hg.$
Iodide of hydrargyromethylium . .	$(C_2H_3)Hg\,I.$

It is generally admitted, that when a body becomes conjugated, its essential chemical character is not altered by the presence of the conjunct : thus for instance, the series of acids $C_nH_nO_4$, formed by the conjunction of the radicals $C_nH_{(n+1)}$ with oxalic acid, have the same neutralizing power as the original oxalic acid; and, therefore, if we assume the organo-metallic bodies above mentioned to be metals
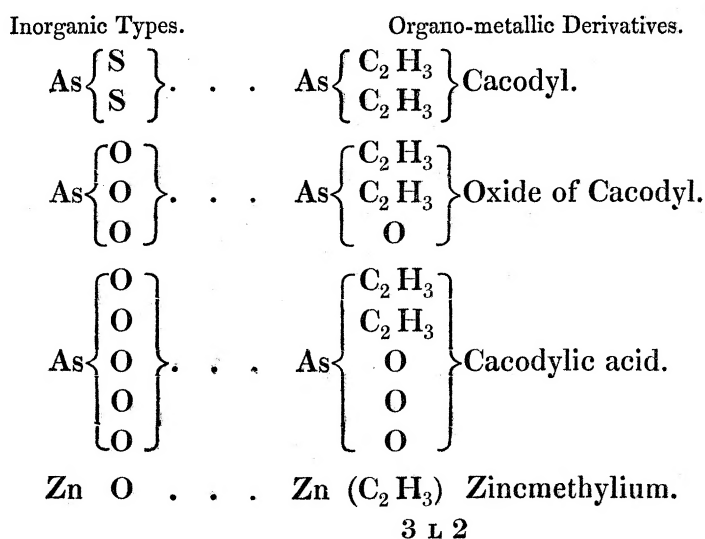
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* Journal of the Chemical Society, vol. iii. p. 372.

conjugated with various hydrocarbons, we might reasonably expect, that the chemical relations of the metal to oxygen, chlorine, sulphur, &c. would remain unchanged; a glance at the formulæ of these compounds will however suffice to show us that this is far from being the case: it is true that cacodyl forms protoxide of cacodyl and cacodylic acid, corresponding the one to a somewhat hypothetical protoxide of arsenic, which, if it exist, does not seem to possess any well-defined basic character, and the other to arsenious acid; but no compound corresponding to arsenic acid can be formed, and yet it cannot be urged that cacodylic acid is decomposed by the powerful reagents requisite to procure further oxidation, for concentrated nitric acid may be distilled from cacodylic acid without decomposition or oxidation in the slightest degree; the same anomaly presents itself even more strikingly in the case of stanethylium, which, if we are to regard it as a conjugate radical, ought to combine with oxygen in two proportions at least, to form compounds corresponding to protoxide and peroxide of tin; now stanethylium rapidly oxidizes when exposed to the air and is converted into pure protoxide, but this compound exhibits none of that powerful tendency to combine with an additional equivalent of oxygen, which is so characteristic of protoxide of tin; nay, it may even be boiled with dilute nitric acid without evincing any signs of oxidation : I have been quite unable to form any higher oxide than that described; it is only when the group is entirely broken up and the ethyl separated, that the tin can be induced to unite with another equivalent of oxygen. Stibethyl also refuses to unite with more or less than two equivalents of oxygen, sulphur, iodine, &c., and thus forms compounds, which are not at all represented amongst the combinations of the simple metal antimony.

When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivs. of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, &c.; and in the five-atom group NO_5, NH_4O, NH_4I, PO_5, PH_4I, &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms. It was probably a glimpse of the operation of this law amongst the more complex organic groups, which led LAURENT and DUMAS to the enunciation of the theory of types; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts,—had they not assumed, that the properties of an organic compound are dependent upon the position and not upon the nature of its single

atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done; such an assumption could only have been made at a time when the data upon which it was founded were few and imperfect, and, as the study of the phenomena of substitution progressed, it gradually became untenable, and the fundamental principles of the electro-chemical theory again assumed their sway. The formation and examination of the organo-metallic bodies promise to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcileable; for, whilst it is evident that certain types of series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electro-chemical character of its single atoms, and not merely upon the relative position of those atoms. Let us take, for instance, the compounds formed by zinc and antimony; by combination with 1 equiv. of oxygen the electro-positive quality of the zinc is nearly annihilated; it is only by the action of the highly oxidizing peroxide of hydrogen that the metal can be made to form a very unstable peroxide; but when zinc combines with 1 equiv. of methyl or ethyl, its positive quality, so far from being neutralized, is exalted by the addition of the positive group, and the compound now exhibits such intense affinity for the electro-negative elements as to give it the property of spontaneous inflammability. Teroxide of antimony has also little tendency to pass into a higher state of oxidation; but when its three atoms of oxygen are replaced by the electro-positive ethyl, as in stibethine, that affinity is elevated to the intense degree which is so remarkable in this body.

Taking this view of the so-called conjugate organic radicals, and regarding the oxygen, sulphur or chlorine compounds of each metal as the true molecular type of the organo-metallic bodies derived from it by the substitution of an organic group for oxygen, sulphur, &c., the anomalies above mentioned entirely disappear, and we have the following inorganic types and organo-metallic derivatives:—

Inorganic Types.   Organo-metallic Derivatives.

$$\text{As}\begin{Bmatrix} S \\ S \end{Bmatrix} \quad \cdots \quad \text{As}\begin{Bmatrix} C_2H_3 \\ C_2H_3 \end{Bmatrix}\text{Cacodyl.}$$

$$\text{As}\begin{Bmatrix} O \\ O \\ O \end{Bmatrix} \quad \cdots \quad \text{As}\begin{Bmatrix} C_2H_3 \\ C_2H_3 \\ O \end{Bmatrix}\text{Oxide of Cacodyl.}$$

$$\text{As}\begin{Bmatrix} O \\ O \\ O \\ O \\ O \end{Bmatrix} \quad \cdots \quad \text{As}\begin{Bmatrix} C_2H_3 \\ C_2H_3 \\ O \\ O \\ O \end{Bmatrix}\text{Cacodylic acid.}$$

$$\text{Zn} \quad O \quad \cdots \quad \text{Zn} \ (C_2H_3) \quad \text{Zincmethylium.}$$

Inorganic Types.　　　　　　Organo-metallic Derivatives.

$$Zn\begin{Bmatrix} O \\ O_x \end{Bmatrix} \ldots \quad Zn\begin{Bmatrix} C_2H_3 \\ O_x \end{Bmatrix} \text{Oxide of Zincmethylium.}$$

$$Sb\begin{Bmatrix} O \\ O \\ O \end{Bmatrix} \ldots \quad Sb\begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{Bmatrix} \text{Stibethine.}$$

$$Sb\begin{Bmatrix} O \\ O \\ O \\ O \\ O \end{Bmatrix} \ldots \quad Sb\begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \\ O \end{Bmatrix} \text{Binoxide of Stibethine.}$$

$$Sb\begin{Bmatrix} O \\ O \\ O \\ O \\ O \end{Bmatrix} \ldots \quad Sb\begin{Bmatrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \end{Bmatrix} \text{Oxide of Stibethylium.}$$

$$Sn \ O \quad \ldots \quad Sn \ (C_4H_5) \ \text{Stanethylium.}$$

$$Sn\begin{Bmatrix} O \\ O \end{Bmatrix} \ldots \quad Sn\begin{Bmatrix} C_4H_5 \\ O \end{Bmatrix} \text{Oxide of Stanethylium.}$$

$$Hg\begin{Bmatrix} I \\ I \end{Bmatrix} \ldots \quad Hg\begin{Bmatrix} C_2H_3 \\ I \end{Bmatrix} \text{Iodide of Hydrargyromethylium.}$$

The only compound which does not harmonize with this view is ethostibylic acid, to which Löwig assigns the formula $C_4 H_5 Sb O_5$; but as that chemist has not yet fully investigated this compound, it is possible that further research may satisfactorily elucidate its apparently anomalous composition.

It is obvious that the establishment of this view of the constitution of the organometallic bodies will remove them from the class of organic radicals, and place them in the most intimate relation with ammonia and the bases of WURTZ, HOFMANN and PAUL THENARD; indeed, the close analogy existing between stibethine and ammonia, first suggested by GERHARDT, has been most satisfactorily demonstrated by the behaviour of stibethine with the haloid compounds of methyl and ethyl. Stibethine furnishes us, therefore, with a remarkable example of the operation of the law of symmetrical combination above alluded to, and shows, that the formation of a five-atom group from one containing three atoms, can be effected by the assimilation of two atoms, either of the same, or of opposite electro-chemical character: this remarkable circumstance suggests the following question:—Is this behaviour common also to the corresponding compounds of arsenic, phosphorus and nitrogen; and can

the position of each of the five atoms, with which these elements respectively combine, be occupied indifferently by an electro-negative or an electro-positive element? This question, so important for the advance of our knowledge of the organic bases and their congeners, cannot now long remain unanswered.

If the views which I have just ventured to suggest should be as well borne out by future researches as they are by the facts already known, they must occasion a profound change in the nomenclature of the extensive series of compounds affected by them: I have not, however, ventured to introduce this new system of nomenclature, even in the case of the new bodies described in this memoir, since hasty changes of this kind, unless absolutely necessary, are always to be deplored. In accordance with the suggested view of the constitution of the organo-metallic compounds, the following plan of nomenclature would probably be found most convenient.

Arsenic Compounds.

$(C_2 H_3)_2 As$	Bimethide of arsenic.
$(C_2 H_3)_2 AsO$	Bimethoxide of arsenic.
$(C_2 H_3)_2 As\ O_3$	Bimetharsenic acid.
$(C_2 H_3)_2 As\ O_3 + KO$ . . .	Bimetharseniate of potash.

Zinc Compounds.

$(C_2 H_3)Zn$	Methide of zinc.
$(C_4 H_5)Zn$	Ethide of zinc.
$(C_{10} H_{11})Zn$	Amylide of zinc.

Tin Compounds.

$(C_2 H_3)Sn$	Methide of tin.
$(C_2 H_3)SnI$	Methiodide of tin.
$(C_4 H_5)Sn$	Ethide of tin.
$(C_4 H_5)SnO$	Ethoxide of tin.
$(C_4 H_5)SnCl$	Ethochloride of tin.
$(C_4 H_5)SnOSO_3$	Sulphate of ethoxide of tin.
$(C_{10} H_{11})Sn$	Amylide of tin.
$(C_{10} H_{11})SnO$	Amyloxide of tin.

Antimony Compounds.

$(C_2 H_3)_3 Sb$	Termethide of antimony.
$(C_2 H_3)_4 SbO$	Quadromethoxide of antimony.
$(C_4 H_5)_3 Sb$	Terethide of antimony.
$(C_4 H_5)_3 Sb\ O_2$	Terethobinoxide of antimony.

Mercury Compounds.

$(C_2 H_3)Hg$ . . . . . . Methide of mercury.

$(C_2 H_3)HgI$ . . . . . Methiodide of mercury.

In naming the new bodies described in the present paper, I have, in conformity with the nomenclature of the organic bases, adopted the principle of employing the termination "*ium*" when the body unites with one equivalent of oxygen, chlorine, sulphur, &c., like ammonium, and the terminal "*ine*" when, like ammonia, it combines with two additional atoms.